PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Luminescent Material

We, THE BRITISH THOMSON-HOUSTON COMPANY LIMITED, a British Company, having its registered office at Crown House, Aldwych, London, W.C.2, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to luminescent materials consisting of Ba, Mg, Si, O and Mn with or without chlorine, the Mn being present in a small quantity and serving as an activator.

A luminescent material, according to one feature of the invention, is made by a process which consists in heating together at a temperature of between 1040° C. and 1060° C. in an oxidising atmosphere an intimate mixture of BaO, MgO, SiO_2 (or compounds of Ba, Mg and Si which under the prevailing conditions break down to produce the desired reaction oxides), and a manganese compound, with or without a source of chlorine for a period of at least one hour and then reducing the resulting product to powder, the molecular proportions of BaO to MgO lying between 3:2 and 1:2, every molecule of BaO being associated with between 2 and 3 mols of SiO_2, and every mol of MgO being associated with between ½ and 1 mol of SiO_2, the molecular proportions of Mn lying between 1 and 15 mols percent of the total BaO and MgO.

According to a further feature of the invention a luminescent material consisting of barium-magnesium-silicate activated with manganese, is prepared by heating together at a temperature of between 1040° C. and 1060° C. in an oxidising atmosphere, an intimate mixture of BaO, $BaCl_2$, MgO, SiO_2 and $MnCO_3$, and then reducing the resulting product to powder.

A further method of preparing a luminescent material consisting of barium-magnesium-silicate activated with manganese, according to the invention, consists in preparing a barium di-silicate by co-precipitation from a solution of aqueous ammoniacal $Ba(OH)_2$ and alcoholic tetra-ethyl-silicate, intimately mixing the precipitate with MgO, SiO_2 and $MnCl_2.4H_2O$, and heating the mixture in an oxidising atmosphere at a temperature of between 1040° C. and 1060° C. for periods of from 1 to 12 hours with intermediate grindings between the heating steps.

The resultant material may also contain a small proportion of chlorine arising from the use of $MnCl_2$ as the compound from which the activator is introduced, the use of the chloride of manganese having been found greatly to facilitate the formation of the material. Alternatively, a mixture of BaO, MgO, $BaCl_2$, SiO_2 and $MnCO_3$ may be used. In this case the chlorine is supplied by $BaCl_2$ which has replaced some of the BaO abovementioned. Other sources of chlorine may be used such as NH_4Cl, $MgCl_2$ and the like, but these offer no advantages over $BaCl_2$. For convenience $BaCl_2.2H_2O$ may be used. Other Mn compounds which do not adversely affect the phosphor may be used as the source of Mn.

The preferred luminescent material of the invention consists of barium-magnesium-silicate activated with manganese, the molecular proportion of BaO to MgO being 3:2, said material containing no other constituents (except for unavoidable impurities) than excess silica and chlorine, chlorine (if present) being limited to 0.1 per cent, by weight, of the total material.

The colour of the radiation is green when excited either by cathode rays or by long and short wave U.V. radiation, and little or no phosphorescence is produced.

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The material of the invention is conveniently prepared by heating together an intimate mixture of a precipitate having the approximate formula $BaSi_2O_5$ (hereinafter referred to as the barium di-silicate precipitate), prepared by co-precipitation of solutions of aqueous ammoniacal $Ba(OH)_2$ and alcoholic pure tetra-ethyl-silicate, with appropriate amounts of MgO, SiO_2 and $MnCl_2.4H_2O$, the last conveniently as a 50% aqueous solution. The heating should be effected in silica crucibles in an oxidising atmosphere for periods of 1 to 12 hours at a temperature of between 1040° C. and 1060° C., with intermediate grinding between firings.

The barium di-silicate precipitate, consisting of BaO.2.4 to 2.5 SiO_2 which may be partly as a compound and partly as a mix of $BaO+SiO_2$, or nearly all one way or the other, when fired, produces the compound $BaSi_2O_5$ with presumably some excess SiO_2 either incorporated in the crystals or as an intercrystalline admixture.

When a green-luminescent material is desired, the range of the content of manganese based on the use of $MnCl_2.4H_2O$ as the source of manganese preferably lies between 1 and 15% molecular reckoned on the total molecular content of BaO and MgO. The preferred amount of $MnCl_2.4H_2O$ should lie between 4 and 5 mols per cent of the mol total of BaO and MgO. For a red-luminescent material, approximately the same limits apply, but the optimum amount is less critical.

When the green-luminescent material is to be prepared, the best results are obtained with a high BaO:MgO molecular ratio, 3 BaO:2MgO giving good results.

When the 3:2 BaO:MgO mol ratio is used, and the "$BaSi_2O_5$ precipitate" abovementioned, the amount of SiO_2 to MgO lies between 1:2 and 1:1 on a molecular basis. High proportions of SiO_2 may be used, but this has a deleterious effect on the luminescence.

Instead of the "$BaSi_2O_5$ precipitate", appropriate amounts of $BaCO_3$ and SiO_2, or $BaCO_3$ and silicic acid, or other suitable Ba compounds may be used.

When $BaCl_2.2H_2O$ is used as the source of the chlorine, the amount of "$BaSi_2O_5$ precipitate" replaced by $BaCl_2.2H_2O+SiO_2$ should not exceed 20% of the $BaSi_2O_3$ on a molecular basis and should preferably be about 5%.

When another manganese compound is substituted for the $MnCl_2.4H_2O$, this should be done on an equivalent Mn basis.

All materials should be at least of Analytical Reagent Purity, and the MgO and SiO_2 should preferably be of purity, fineness and reactivity such as is normally associated with the preparation of luminescent materials. Allowance should be made for the moisture etc. content of all the raw materials.

We will now describe two examples of the method of preparation of green and red luminescing materials according to the invention.

EXAMPLE I.

Preparation of the green luminescent material: Mix intimately together, by ball milling or other convenient means:—

27.8 gms. Ba di-silicate precipitate (containing 7.5% volatile matter)
2.5 gms. MgO containing 97.7% MgO
5.0 gms. SiO_2 containing 95.6% SiO_2, and
1.25 gms. $MnCl_2.4H_2O$ (as a 50% w.v. solution in water)

Fire in a silica crucible or crucibles in an atmosphere of air at 1050° C. ± 10° C. for periods of 1, 2 and 4 hours successively, with intermediate grinding and mixing between.

The luminescence develops fully in the third firing and the resultant material should appear very nearly white by daylight.

EXAMPLE II.

Preparation of the green luminescent cent material proceed similarly to Example I, but use the following amounts of the ingredients:—

7.8 gms. Ba di-silicate precipitate, containing 7.5% moisture
8.3 gms. MgO containing 97.7% MgO
12.6 gms. SiO_2 containing 95.6% SiO_2 and
1.2 gms. $MnCl_2.4H_2O$

Fire for 1 hour at 1050° ± 10° C. as before, followed by a second firing for 2 hours at the same temperature, with intermediate grinding.

WHAT WE CLAIM IS:—

1. A method of preparing a luminescent material consisting of barium-magnesium-silicate activated with manganese, which consists in heating together at a temperature of between 1040° C. and 1060° C. in an oxidising atmosphere an intimate mixture of BaO, MgO, SiO_2 (or compounds of Ba, Mg and Si which under the prevailing conditions break down to produce the desired reaction oxides), and a manganese compound, with or without a source of chlorine, for a period of at least one hour and then reducing the resulting product to powder, the molecular proportions of BaO to MgO lying between 3:2 and 1:2, every molecule of BaO being associated with between 2 and 3 mols of SiO_2, and every mol of MgO being associated with between ½ and 1 mol of SiO_2, the molecular proportions of Mn lying between 1 and 15 mols per cent of the total BaO and MgO.

2. A method as claimed in Claim 1, in which the source of chlorine is provided by using $MnCl_2$ as the manganese compound.

3. A method as claimed in Claim 1, in which the source of chlorine is provided by using $BaCl_2$ in partial substitution for BaO.

4. A method of preparing a luminescent material consisting of barium-magnesium-

silicate activated with manganese, which consists in heating together at a temperature of between 1040° C. and 1060° C. in an oxidising atmosphere, an intimate mixture of BaO, $BaCl_2$, MgO, SiO_2 and $MnCO_3$, and then reducing the resulting product to powder.

5. A method of preparing a luminescent material consisting of barium-magnesium-silicate activated with manganese, which consists in preparing a barium di-silicate by co-precipitation from a solution of aqueous ammoniacal $Ba(OH)_2$ and alcoholic tetra-ethyl-silicate, intimately mixing the precipitate with MgO, SiO_2 and $MnCl.4H_2O$, and heating the mixture in an oxidising atmosphere at a temperature of between 1040° C. and 1060° C. for periods of from 1 to 12 hours with intermediate grindings between the heating steps.

6. A method of preparing a luminescent material as claimed in Claim 5, wherein the molecular ratio of SiO_2 to MgO lies between 1:2 and 1:1 when the ratio of BaO:MgO is 3:2 on a molecular basis.

7. A method of preparing a luminescent material as claimed in Claim 5, wherein in order to introduce chlorine into the material, up to 20% molecular of the barium di-silicate precipitate is replaced by $BaCl_2.2H_2O$ and silica, the $MnCl_2.4H_2O$ being replaced by $MnCO_3$.

8. A luminescent material consisting of barium-magnesium-silicate activated with manganese, the molecular proportion of BaO to MgO being 3:2, said material containing no other constituents, except for unavoidable impurities, than excess silica and chlorine, chlorine (if present) being limited to 0.1 per cent, by weight, of the total material.

9. The preparation of a barium magnesium silicate activated with manganese according to Example I or to Example II hereinbefore described.

10. A barium-magnesium-silicate activated with manganese when prepared according to any one of the methods claimed in Claims 1 to 7.

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PROVISIONAL SPECIFICATION

Luminescent Material

We, THE BRITISH THOMSON-HOUSTON COMPANY LIMITED, a British company having its registered office at Crown House, Aldwych, London, W.C.2, do hereby declare this invention to be described in the following statement:—

This invention relates to luminescent materials, and consists in a luminescent material composed of Ba, Mg, Si, O and Mn, the Mn being present in a small quantity and serving as an activator. The improved luminescent material of the invention may be regarded as a barium-magnesium silicate activated with manganese, an intimate mixture of the compounds from which the material is prepared being heated together in order to effect a reaction between them.

The luminescent material may be prepared by heating together an intimate mixture of BaO, MgO, SiO_2 and $MnCl_2$, when these are used in the correct proportions. The resultant material may also contain a small proportion of chlorine arising from the use of $MnCl_2$ as the compound from which the activator is introduced, the use of the chloride of manganese is found greatly to facilitate the formation of the compound. Alternatively a mixture of BaO, MgO, $BaCl_2$, SiO_2 and $MnCO_3$ may be used. In this case the chlorine is supplied by $BaCl_2$ which has replaced some of the BaO above-mentioned. Other sources of chlorine may be used such as NH_4Cl, $MgCl_2$ and the like but these offer no advantage over $BaCl_2$. For convenience $BaCl_2.2H_2O$ may be used. Other Mn compounds which do not adversely affect the phosphor may be used as the source of Mn.

When the molecular ratio of BaO:MgO is high, e.g. from 4:3 to 1:2, the colour of the radiation is green when excited by cathode rays and by long and short wave U.V. radiation and there appears to be little or no phosphorescence. When the BaO:MgO ratio is low, i.e. about 1:8, the luminescence is red, and is only excited by cathode rays. In this case there is some phosphorescence. Intermediate ratios give mixed reds and greens, and yellows.

The materials are conveniently prepared by heating together an intimate mixture of a precipitate having the approximately formula $BaSi_2O_5$, prepared by co-precipitation of solutions of aqueous ammoniacal $Ba(OH)_2$ and alcoholic pure tetra-ethyl silicate and appropriate amounts of MgO, SiO_2 and $MnCl_2$ $4H_2O$, the latter conveniently as a 50% aqueous solution, in silica crucibles in an atmosphere of air for periods of 1 to 12 hours at a temperature of about 1050° C., with intermediate grinding between firings.

The Mn content is fairly critical, especially with the green luminescent material, and the preferred amount of $MnCl_2.4H_2O$ is between 4 and 5% by weight, of the total of $BaO+MgO+SiO_2$. Limits between which fluorescence is visible are approximately 1 to 15% $MnCl_2.4H_2O$ on the previous basis. For the red luminescent material, the same

limits approximately apply, but the optimum amount is less critical.

When the green-luminescent material is to be prepared, the best results are obtained with a high BaO.MgO molecular ratio, 3BaO to 2MgO giving good results.

When the 3:2 BaO.MgO mol ratio is used, and the $BaSi_2O_5$ precipitate above-mentioned, the amount of SiO_2 to MgO should lie between 1:2 and 2:1 on a molecular basis. High proportions of SiO_2 may be used, but this has a deleterious effect on the luminescence.

Instead of the $BaSi_2O_5$ precipitate, appropriate amounts of $BaCO_3$ and SiO_2, or $BaCO_3$ and silicic acid, or other suitable Ba compounds may be used.

When $BaCl_2.2H_2O$ is used as the source of the chlorine, the amount of $BaSi_2O_5$ precipitate replaced by $BaCl_2.2H_2O+SiO_2$ should not exceed 20% of the $BaSi_2O_5$ on a molecular basis and should preferably be about 5%.

When another manganese compound is substituted for the $MnCl_2.4H_2O$, this should be done on an equivalent Mn basis.

All materials should be at least of analytical reagent purity, and the MgO and SiO_2 should preferably be of a purity, fineness and reactivity such as is normally associated with the preparation of luminescent materials. Allowance should be made for the moisture etc. content of all the raw materials.

We will now describe two examples of the method of preparation of green and red luminescing materials according to the invention.

EXAMPLE I.

Preparation of the green luminescent material: Mix intimately together, by ball milling or other convenient means:—

27.8 gms. Ba di-silicate precipitate (containing 7.5% moisture etc)
2.5 gms. MgO containing 97.7% MgO
5.0 gms. SiO_2 containing 95.6% SiO_2 and
1.25 gms. $MnCl_2.4H_2O$

Fire in a silica crucible or crucibles in an atmosphere of air for periods of 1, 2 and 8 to 16 hours, successively, with intermediate grinding and mixing between.

The luminescence develops fully in the third firing and the resultant material should appear very nearly white by daylight.

EXAMPLE II.

To prepare the red luminescent material proceed similarly to Example I, but use the following amounts of the ingredients:—

7.8 gms. Ba di-silicate precipitate, containing 7.5% moisture etc.
8.3 gms. MgO containing 97.7% MgO
12.6 gms. SiO_2 containing 95.6% SiO_2 and
1.2 gms. $MnCl_2.4H_2O$

Fire only for 1 hour plus 2 hours at 1050° C.

X-ray examination of the resulting luminescent materials has shown that two distinct materials or phases are produced according to the proportions of BaO and MgO which are used in the preparation of the material; both phases are believed to be barium-magnesium silicates. The first phase, called A for convenience, which gives the green luminescence, exists over an approximate range of molecular BaO.MgO ratios from 4:3 to 1:2, the second phase exists at an approximate molecular BaO.MgO ratio of 1:8 and gives red luminescence with cathode rays only. Between 100% BaO and 4BaO.3MgO a mixture of $BaSi_2O_5$ (barium di-silicate) and material of the first phase is present, dependent on the amount of MgO present. Between 1BaO. 2MgO and 1BaO.8MgO materials of both phases appear mixed, and with no BaO present Mg_2SiO_4 or $MgSiO_3$ appear according to the amount of SiO_2 available to the MgO.

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